PATENT SPECIFICATION 1273 225

DRAWINGS ATTACHED

(21) Application No. 45982/69 (22) Filed 18 Sept. 1969
(31) Convention Application No. P 17 95 358.1
(32) Filed 19 Sept. 1968 in
(33) Germany (DT)
(45) Complete Specification published 3 May 1972
(51) International Classification B29C 5/00 C08G 20/10
(52) Index at acceptance B5A 1R14C1A

1273225

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(54) IMPROVEMENTS IN AND APPARATUS FOR THE PRODUCTION OF POLYAMIDE MOLDINGS

(71) We, BADISCHE ANALIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process and apparatus for the production of polyamide moldings by activated anionic polymerization of lactams in a mold.

Activated anionic polymerization of lactams in a mold can be carried out most simply by mixing a catalyst and activator into a melt of the lactam to be polymerized in a mold. In this case the mixture does not have to be transferred from one vessel to another and solidifies immediately in the shape which the molding is to have. This method has disadvantages particularly in the production of large and long moldings such as rods, long plates or articles of intricate shape. It is difficult in these cases to incorporate the catalyst and activator homogenously in the lactam to be polymerized. In such cases therefore, the mixed starting materials are allowed to flow into the mold or the starting materials are mixed during introduction through a mixing nozzle.

Such a method also has disadvantages. During pouring of the melt, air bubbles are introduced into the melt and give flaws in the molding even when the lower end of the inflow pipe for the starting materials extends below the surface of the polymerizing lactam melt in the mold. Another disadvantage is that residues of polymerizing lactam mixture remain in the inflow pipe, polymerize therein and in the course of time clog the pipe.

We have now found that the production of polyamide moldings by activated anionic polymerization of lactams in a mold in which a lactam melt containing activator and a lactam melt containing catalyst which have been heated separately to polymerization temperature are supplied to the mold, mixed and allowed to polymerize, the melt being introduced into the mold beneath the surface of the polymerization mixture, can be carried out without the said disadvantages when the two melts are forced through two separate heated pipes completely filled with the melt into the polymerizing mixture.

Apparatus for carrying out the process may comprise a mold, two reservoirs for lactam each provided with means for heating and cooling the contents and for mixing the lactam therein with a catalyst or activator, a separate pipeline provided with a pump and capable of being heated arranged to lead molten lactam containing catalyst or activator (as the case may be) from each of the two reservoirs to a pourer comprising two heatable pipes, a horizontally directed nozzle located at the lower end of each heatable pipe for the introduction of molten lactam material from the pipe into the mold at a level beneath the surface level of polymerizing material therein, and two valves, one provided between each pipe and the corresponding nozzle in the pourer, each valve being adapted to open in response to the pressure in the corresponding pipe, whereby the pipes can be maintained completely filled with molten lactam material.

The pumps used may be commercial pumps such as gear pumps, rotary pumps, diaphragm pumps or piston pumps.

A particularly advantageous embodiment of the pourer is shown in Figure 1. Feed pipes 1a and 1b (which are surrounded by a heating jacket 2 fitted with an inlet and outlet for hot steam) each bears at its lower end a pourer head 3a or 3b rotatable about its vertical axis and provided at its lower end with a nozzle 4a or 4b which is not directed upwards and is preferably directed horizontally.

Figure 2 shows by way of example an embodiment of a pourer head in which a spring-loaded pressure valve is provided between the mouth of the supply pipe and the nozzle.

Instead of the pressure valve shown in

Figure 2, however, all other suitable types of valve may be used, provided the sealing element does not adjoin too large a space that could prevent the power from being completely filled with liquid. This will prevent (a) unintentional discharge of melt and (b) rising of the polymerizing mixture back into the supply pipe.

The pourer heads may be turned about their vertical axis and fixed in any position. They are preferably adjusted so that jets of melt issuing horizontally from the nozzles intersect at an angle of from 30° to 180°, preferably from 60° to 120°. The nozzles are of such a size that the melts can issue at a flow velocity of 20 to 200 cm/sec, preferably 50 to 150 cm/sec.

In filling molds of special shapes it may be advantageous to direct the streams of starting mixtures not exactly horizontally but at an acute angle to the horizontal.

Complete filling of the supply pipes (closed at their ends with valves) with liquid makes it possible to supply the liquid starting mixtures without even the slightest trace of air bubbles passing into the polymerizing mixture. It is advantageous to use fairly narrow supply pipes in which the starting mixtures flow at a velocity of from 20 to 200 cm/sec.

Lactams having at least six rings carbon atoms are particularly suitable for the process according to this invention; specific examples are caprolactam, enantolactam, capryllactam, capric lactam, laurolactam or carbon-substituted derivatives of these lactams, such as 3 - methylcaprolactam and 4 - isopropylcaprolactam. It is preferred to use caprolactam. Mixtures of the said lactams may also be used. The said lactams may also contain small amounts (generally from 0.1 to 5 mole % of the said lactams) of other lactams which are connected to each other by bridges, for example methylene - bis - caprolactam.

In addition to generally known polymerization catalysts, alkali metal lactams such as are described in German Patent Specification No. 1,067,587 are particularly suitable. They are used in amounts of from 0.01 to 10% by weight, preferably from 0.1 to 5% by weight, with reference to the total weight of the polyamide-forming starting materials. However, it is also possible to use amounts outside these ranges for special purposes. Naturally mixtures of these catalysts in any proportions are also suitable.

Known substances, for example N - acyllactams, isocyanates, N - cyanolactams, substituted ureas and reaction products of carbamyl chlorides with heterocycles such as imidazole are suitable as activators. Bis - (lactam - N - carbonylamino) - alkanes such as can be prepared by reaction of 2 moles of lactam with 1 mole of an aliphatic diisocyanate, are very suitable. These substances are used in amounts of 0.05 to 10%, preferably 0.1 to 5%, by weight with reference to the total weight of the polyamide - forming starting materials.

Reinforcing materials, fillers, lubricants, delustring agents or stabilizers may be used as additives in the process according to this invention provided their particle size is correlated to this process. For example metal powders such as aluminum r copper powder, ground shale and diatomaceous earth are suitable as fillers. Glass fibers or other fibers are suitable as reinforcement materials provided they are so fine that they do not prevent closing of the valves.

The mode of operation of the apparatus and the process according to this invention will now be described in greater detail.

It is advantageous in carrying out the process to halve the amount of lactam to be polymerized, introduce the halves into reservoirs, melt them therein and dissolve in one half of the melt the catalyst (reservoir 1) and in the other half the activator for the anionic lactam polymerization (reservoir 2). The activator and catalyst may however be dissolved in unequal portions of lactam, the metering then being regulated so that the polymerization mixture contains the calculated amounts of catalyst and activator.

The choice of activator and catalyst depends on the shape of the molding to be made, on the rate of delivery of the pumps used and on the desired polymerization temperature and rate of polymerization.

Activator and catalyst are incorporated in the separate lactam melts at temperatures of from 95° to 170°C, depending on the type used. The temperature of the melt containing catalyst is preferably kept at from 90° to 120°C, that of the melt containing activator preferably at from 110° to 135°C.

The melt containing catalyst and the melt containing activator are withdrawn from the reservoirs in the separate pipelines (previously well evacuated), for example by gravitation or by pump pressure.

The pipelines for the lactam melts are heated to temperatures above the melting point of the lactam to be polymerized, advantageously to a temperature of from 90° to 140°C according to the activator-catalyst system chosen.

The pourer to be used according to the invention is heated to a temperature above the melting point of the lactam to be polymerized and filled with liquid by tentative pumping of the starting material for the anionic polymerization. Then the pourer is lowered to the bottom of the mold in which polymerization is to take place, the starting materials are pumped in slowly at first until the nozzles are immersed to a depth of 2 to 3 cm in the polymerizing melt. Then the starting materials are pumped in at full speed and the pourer lifted (or the mold lowered)

at a rate corresponding to the rate of delivery of the pump so that the pourer is immersed in the polymerizing melt to a depth of 3 to 15 cm. As soon as the mold has been filled, the pourer is withdrawn from the polymerizing mixture.

A particular advantage of the process according to this invention consists in the fact that no activator mixture can rise back into the supply pipe for the catalyst mixture (and vice versa) as is unavoidable in the case of mixing nozzles if one of the pumps for the two starting mixtures operates less efficiently or fails or other disturbances occur. When operating for several hours it is advisable to flush the pourer with the starting mixtures each time the casting of a molding has been completed.

The molds to be used are heated to from 80° to 160°C depending on the size of the molding. When preparing long moldings such as rods or long plates, it is preferable to use mold temperatures of from 80° to 120°C.

Heating of the reservoirs for the starting mixtures, the pipelines and the pourer should be correlated so that the starting materials enter the mold at a temperature of from 100° to 140°C, preferably from 110° to 130°C, depending on the activator-catalyst system chosen.

Although it is not absolutely necessary when using the abovementioned preferred activators, the air above the surface of the mixture to be polymerized in the mold may be expelled by means of an inert gas, for example nitrogen.

The process according to the invention is suitable for the production of moldings of any shape, particularly for the production of long and large particles of intricate shape in which shrinkage bubbles form when the starting materials are poured rapidly and intermittently. Round rods, prismatic sections and other sections may be prepared by the process according to this invention with particular advantage.

Moldings made by the process according to this invention are entirely devoid of air bubbles and streaks. Carrying out the process according to the invention will be further illustrated by the following Examples. The parts specified are parts by weight.

EXAMPLE 1

10.6 liters per minute of a mixture, heated to 120°C. of 100 parts of caprolactam and 0.98 parts of sodium caprolactam and 10.6 liters per minute of a mixture, heated to 120°C, of 100 parts of caprolactam and 2.42 parts of 1,6 - bis - (caprolactam - N - carbonylamino) - hexane are continuously pumped through the vertical pourer shown in Figure 1, which is heated to 120°C with steam and provided with two supply pipes for the catalyst mixture and the activator mixture, to the bottom of a cylindrical mold of stainless steel having a diameter of 150 mm and a length of 2.8 meters. The outlets of the valves have cross-section of 3 cm² each and the jets of both starting mixtures are approximately horizontal. The two valves are screwed in so that the liquid jets of the two starting mixtures intersect at about 90°. The starting materials have a temperature in the mold of 120°C at the beginning of the pouring process. During pouring the mold is lowered at a mean rate of 1.2 meters per minute so that the orifices in the valves are always from 7 to 12 cm beneath the surface of the liquid in the mold. After 2.3 minutes, the mold is full, pumping of the starting mixtures is stopped and the mold is lowered to a sufficient extent for the pourer to be above the surface of the polymerizing mixture. While pouring is going on, the anionic lactam polymerization begins at the bottom of the cylindrical mold with the evolution of heat and a rapid, increase in the viscosity of the mixture and proceeds to the surface of the filled mold at about the same speed as the pouring speed. The contents of the mold have completely polymerized into a solid molding within two to three minutes. After another two minutes, the polymerized molding in the mold is heated in a horizontal position in a tubular kiln heated to 120°C, kept for six houre at this temperature and allowed to cool to room temperature within two hours. Then the round rod is removed from the mold. If great importance is attached to a smooth surface, a layer can be removed down to a diameter of 135 mm. A completely smooth homogenous rod of polycaprolactam is obtained which is entirely devoid of flaws, air bubbles and streaks and which has excellent mechanical properties. The polyamide has a high molecular weight since it can only be dissolved incompletely (0.2%) in 96% sulfuric acid. The content of extractable constituents is about 2%, the modulus of elasticity is 41,000 kg/cm² and the elongation is 30%.

Working in the manner described permits the continuous casting of shaped articles one after another without crusts of caprolactam polymer forming on the pourer. When casting is carried on for long periods it is advisable to rinse the pourer with the starting materials for a few seconds from time to time. The said arrangement makes it impossible for the starting materials already in the supply pipelines to mix together and to polymerize prematurely and clog up the system.

EXAMPLE 2

The procedure described in Example 1 is followed but a bold having a diameter of 222 mm is used and the two starting mixtures are pumped into the mold at a rate of 23.2 liters per minutes in each case. The mold is lowered at a rate of 1.2 meters per minute.

The mixing temperature of the starting materials is 118°C. After a layer has been removed, a flawless cylindrical rod of polycaprolactam is obtained having a diameter of 200 mm and a length of 2.6 meters. The fact that it is devoid of flaws may be confirmed (as well as in Example 1) by ultrasonic tests.

WHAT WE CLAIM IS:—

1. A process for the production of moldings from polyamides by activated anionic polymerization of a lactam in a mold, in which process a lactam melt containing catalyst and a lactam melt containing activator are separately heated to polymerization temperature and supplied continuously to the mold, mixed and allowed to polymerize therein, the lactam melts being introduced into the mold beneath the surface of the polymerization mixture, wherein the melt containing catalyst and the melt containing activator are forced simultaneously through two separate, heated pipes completely filled with melt into the polymerizing mixture.

2. A process as claimed in claim 1 wherein the melts are introduced into the polymerizing mixture in the form of jets which intersect at an angle of from 60° to 120°.

3. A process as claimed in claim 2 wherein the jets are horizontal or substantially horizontal.

4. A process as claimed in any of claims 1 to 3 wherein the melts are introduced at a velocity of from 20 to 200 cm/sec.

5. A process as claimed in claim 4 wherein the said velocity is from 50 to 150 cm/sec.

6. A process as claimed in any of claims 1 to 5 wherein the lactam used is caprolactam.

7. A process as claimed in claim 1 carried out substantially as described in either of the foregoing Examples.

8. Apparatus for the production f moldings from polyamides by activated anionic polymerization of a lactam, comprising a mold, two reservoirs for lactam each provided with means for heating and cooling the contents and for mixing the lactam therein with a catalyst or activator, a separate pipeline provided with a pump and capable of being heated arranged to lead molten lactam containing catalyst or activator (as the case may be) from each of the two reservoirs to a pourer comprising two heatable pipes, a horizontally directed nozzle located at the lower end of each heatable pipe for the introduction of molten lactam material from the pipe into the mold at a level beneath the surface level of polymerizing material therein, and two valves, one provided between each pipe and the corresponding nozzle in the pourer, each valve being adapted to open in response to the pressure in the corresponding pipe, whereby the pipes can be maintained completely filled with molten lactam material.

9. Apparatus as claimed in claim 8 substantially as herein described with reference to the accompanying drawings.

10. Moldings when produced by a process as claimed in any of claims 1 to 7 or by use of an apparatus as claimed in claim 8 or 9.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1273225 COMPLETE SPECIFICATION
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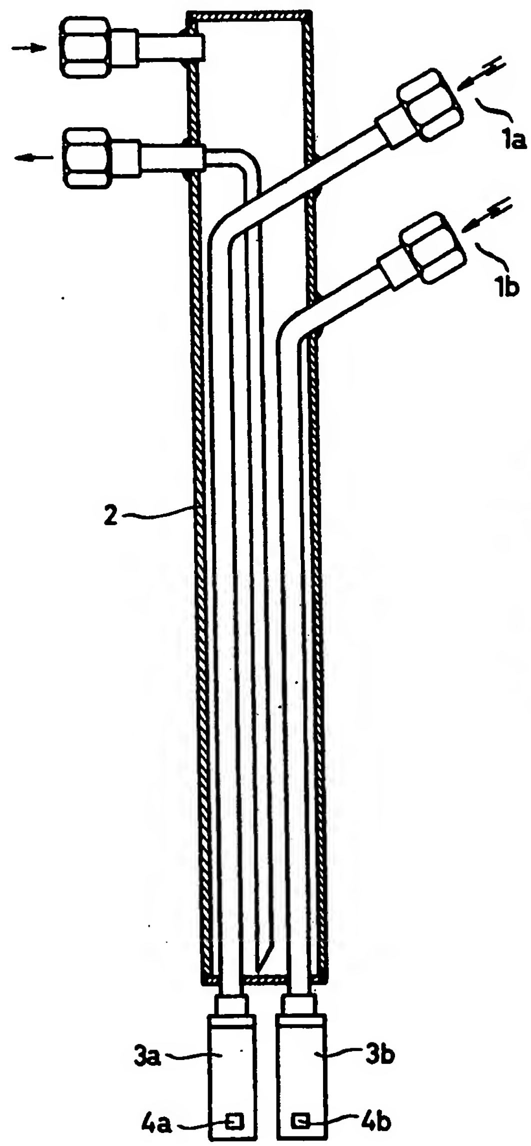

Fig.1

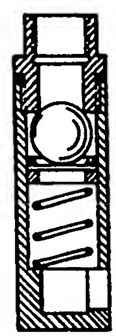

Fig.2